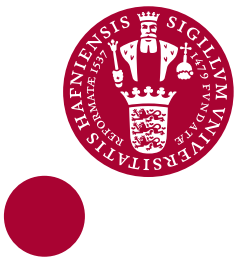

Fate of pesticides in the humid tropics - application to insecticides used in vegetable crops

Chai, Lian Kuet

Publication date:
2008

Document version
Publisher's PDF, also known as Version of record

Abstract

Part 1: Literature review - Fate of pesticides in humid tropical soils and comparison with temperate soil

The humid tropical climate has high humidity, temperature and rainfall which are very conducive for proliferation of pests and diseases. Pesticides are applied on crops and soil throughout the year as crops are cultivated all year round. In the humid tropics, most farms are not fallowed after a crop has been harvested due to limited arable land and animal manures are often used to fertilize the crop. Both practices contribute to the spread of pests and diseases. Consequently, farmers use higher concentrations and increase application frequencies of pesticides. In some instances, cocktails of pesticides are used. Despite extensive use of pesticides in the humid tropics, research on their fate in soils is sparse. This thesis aims to review research works done on the fate of pesticides in humid tropical soils and to compare their sorption, degradation and leaching with those from the temperate regions.

Field dissipation of pesticides in the humid tropical soils is rapid. Fast initial dissipation is attributed to surface losses (runoff, volatilisation, and photodegradation) and leaching, whereas subsequent slower disappearance is related to abiotic and microbial degradation in the soil. Higher precipitation and soil moisture also accelerates the dissipation of pesticides in humid tropical soils. Lower persistency of polar weakly sorbed pesticides such as monocrotophos and methamidophos in soils may be attributed to increased leaching losses and rapid degradation. Pesticides in humid tropical soils appear to leach beyond top soil regardless of their sorption properties. Preferential flow (root channels, macro pores and cracks) caused pesticide leaching regardless of their polarity to leach beyond top soil.

In laboratory studies, faster degradation of pesticides in aerobic humid tropical soils as compared to the anaerobic soil showed that soil microbes play a major role in pesticide degradation. Certain pesticides including acephate have been found to degrade faster in air-dry or field moisture soil than in anaerobic soil and in sterilized soil due to inactivation and absence of soil microorganisms. Slow degradation of some pesticides including paraquat in soils is attributed to its strong binding to soils, protecting it from microbial degradation. The extremely slow degradation of lindane is attributed to their persistent nature. High-dose pesticide treatments (5-fold) in humid tropics appear not to result in pronounced delays of pesticide degradation.

In laboratory studies, paraquat and glyphosate are the most strongly sorbed in humid tropical soils. The least sorbed pesticides are methamidophos and weak acid herbicides. The rest have medium sorption affinity. Sorption of most non-ionic pesticides is well correlated with the content of humic matter. However, for some pesticides such as endosulfan and methamidophos, sorption is also correlated to the contents of clay, while sorption of glyphosate is correlated with the iron and aluminium oxides. The sorption of paraquat, glyphosate, 2,4–D, and lindane appeared not to be significantly affected by

temperature (20 ^{o}C/30 ^{o}C) or pH (4.5/6.5). However, the distribution coefficients for metsulfuron-methyl are inversely correlated with increased soil pH.

In the laboratory, degradation kinetics of pesticides in temperate and tropical soils are very similar as degradation depends on soil properties such as population of soil microorganisms and soil pH. Higher soil temperature causes faster pesticide degradation. Increase in pesticide concentration of 100-fold retards soil microbial activity. Absence of soil microbial activity in sterile soil resulted in comparatively slower pesticides degradation demonstrating that soil microorganisms play a key role in degrading pesticides. In addition, chlorpyrifos degraded faster with increased soil pH.

The sorption of pesticides in temperate and tropical soils is similar. Sorption depends mainly on soil properties especially the contents of organic matter and clay. Less polar pesticides such as chlorpyrifos, permethrin and cypermethrin showed higher sorption than polar pesticides such as acephate and methamidophos. Sorption of chlorpyrifos and permethrin in soil increased with the contents of organic matter in soil whereas the sorption of acephate and cypermethrin was highly correlated with the silt and/or clay content of the soil.

In temperate soils, leaching depends more on soil properties such as organic matter contents, clay and silt. The higher the silt and clay in soil, the higher the acephate is retained. Higher organic matter contents also resulted in higher retention of chlorpyrifos and cypermethrin in the upper layer of soil. However, the presence of macropores which are found abundantly in saturated humid tropical soils may induce preferential flows and this may cause leaching of most pesticides irrespective of their sorption properties.

Research on environmental contamination by pesticides in the humid tropics is still in its infancy. There is a need to conduct more research including leaching of pesticides from single profile to whole catchment, microbial degradation pathways and kinetics, identification of microorganisms responsible for pesticide degradation, enhanced degradation in soils and transport modelling using the local climatic data.

Part 2: Fate of pesticides in crops and soils of Malaysia

Five papers have been written for publication in this PhD. project.

In Paper 1 entitled ‘Method for the determination of cypermethrin in Sarawak soils’, a gas chromatographic method has been developed to determine cypermethrin residues in top and subsoil horizons of three types of Sarawak soils, viz. Semongok (*Paleudults*), Tarat (*Udorthents*) and Balai Ringin (*Kandiudults*) soils. Fourteen different horizons of top and subsoils varying in contents of clay (6 – 67 %) and soil organic carbon (0.22 – 2.20 %) were used in the study. Soil samples were spiked with cypermethrin at three concentration levels (0.01, 0.1 and 1 mg/kg) and subsequently extracted with hexane and acetone for one hour at room temperature. This was then followed by liquid-liquid extraction with dichloromethane before determination of cypermethrin by GC-ECD. The

recoveries ranged between 80.0 % and 101.2 % with standard deviations ranging between 0.6 % and 9.9 %. It was found that addition of 10 ml of water to 10 gram of soil prior to the extraction improved the recovery substantially. The percent recovery decreased with soil depth and increased clay content. The limits of detection were in the range of 1.1 µg/kg to 5.9 µg/kg.

In Paper 2 entitled 'Determination of chlorpyrifos and acephate in tropical soils and application in dissipation studies', a rapid and accurate method for the extraction and determination of chlorpyrifos and acephate in top and subsoil materials of three soil types in Sarawak has been developed. Soil samples were extracted with ethyl acetate and the pesticides were determined by GC-FPD. High recoveries of 76 - 102 % and 76 - 100 % were obtained for acephate and chlorpyrifos respectively, at fortification levels of 0.01, 0.1 and 1 mg/kg with standard deviations below 9.0 %. The addition of water prior to the extraction was important for obtaining high and reproducible recoveries. The method could detect up to 0.01 mg/kg. For chlorpyrifos, the recoveries were correlated with contents of soil organic matter, clay and soil depths. A field study was conducted using the modified method to measure the degradation kinetics and migration of acephate and chlorpyrifos over a period of 84 days in one of the soils. The degradation of acephate and chlorpyrifos were rapid with half-lives of 2.6 and 19.8 days, respectively. Both pesticides were detected in subsoils 2 h after application with concentrations up to 2.3 mg/kg at the deepest (50 cm) soil layer examined. Subsoil concentrations of acephate were higher than chlorpyrifos and subsoil concentrations of acephate peaked after it had started to degrade in the top soil. The subsoil concentrations of pesticides were attributed to transport with soil particles (chlorpyrifos) and via solution (acephate) through pores and cracks present in the soil profile. The study demonstrated the high mobility of even strongly retained and fast degrading pesticides under tropical humid conditions.

Paper 3 entitled 'Dissipation of acephate, chlorpyrifos, cypermethrin and their metabolites in a humid-tropical vegetable production system'. The dissipation of acephate, chlorpyrifos, cypermethrin, and their metabolites were studied in vegetable crop, green mustard (*Brassica juncea*) and soil. Two treatments, Impact 75 (acephate) and Agent 505 (cypermethrin plus chlorpyrifos) were applied four times at weekly intervals to green mustard after they were transplanted in the field. Dissipation of acephate, chlorpyrifos and cypermethrin in green mustard and topsoils followed first-order kinetics with half-lives between 1.1 and 3.1 days for green mustard and 1.4 to 9.4 days for topsoils (26 ^{o}C). Higher vapour pressure of insecticides and higher rainfall appeared to stimulate dissipation from the vegetable although rainfall has least effect on chlorpyrifos. As compared to temperate areas, dissipation rates of acephate and chlorpyrifos were faster in the vegetable but similar rate was observed for cypermethrin. For compliance with the tolerance level, pre-harvest intervals of 13, 4 and 3 days were required for acephate, chlorpyrifos, cypermethrin and their metabolites, respectively. Two metabolites, methamidophos derived from acephate and 3, 5, 6 - trichloropyridinol (TCP) derived from chlorpyrifos amounted to less than 10 and 25 %, respectively by mass of the parent compound in soil. Vegetable shading probably retarded pesticide degradation in soil. Dissipation of pesticides and their metabolites in vegetable was rapid

and faster than in temperate climates. Degradation rate of pesticides in soil was equal to or slightly faster than in temperate soils.

Paper 4 entitled 'Dissipation and leaching of acephate, chlorpyrifos and their main metabolites in field soils of Malaysia'. Degradation and migration of insecticides, acephate and chlorpyrifos and their primary metabolites, methamidophos and TCP, have been studied in three soils of Malaysia under field conditions. The insecticides were applied to freshly tilled soils at 5.2 g/m^2 and 3.5 g/m^2 for acephate and chlorpyrifos, respectively. The initial concentrations of acephate and chlorpyrifos in topsoils were found to be strongly depended on local climatic conditions, mainly solar radiation. Both pesticides and their metabolites were detected in subsoils at the deepest sampling depth monitored of 50 cm at concentrations up to 2.3 mg/kg. Exceptionally high dissipation rate for weakly sorbed acephate was attributed to extensive leaching via macropore flow which was activated due to high moisture content of the soil, high precipitation and presence of conducting macropores running from below A horizons to at least 1 m depth. Transport of chlorpyrifos and TCP which are both sorb strongly to soil organic matter were attributed to macropore transport with soil particles. The half-lives for acephate in topsoils ranged from 0.4 to 2.6 days while substantially longer half-lives of between 12.6 to 19.8 days were observed for chlorpyrifos. Pesticides and metabolites in subsoils dissipated at similar rates as in topsoils with TCP tended to reach peak concentrations 10 – 20 days after its application.

Paper 5 entitled 'Degradation and mineralization kinetics of acephate in tropical soils of Malaysia'. Acephate degradation has been studied for topsoil materials from three typical Malaysian soil types (*Typic Paleudult*, *Typic Udorthent, Typic Kandiudult*) under the laboratory conditions. Four critical variables have been studied: soil moisture (air-dry, moist (~ field capacity) and wet (~ 60 % gravimetric water content), temperature (15 ^{o}C, 25 ^{o}C and 35 ^{o}C), microbial activity (sterilized and non-sterilized soils) and acephate application rates (5 μg g^{-1} and 25 μg g^{-1} fresh weight). In addition mineralization kinetics using ^{14}C-acephate was performed. First-order kinetics could be used in all cases (r^2 > 0.91). Acephate degraded faster in air-dry soil ($t_{½}$ 8.6 – 10.7 days) and field capacity ($t_{½}$ 10.0 – 16.1 days) than in the wet soil ($t_{½}$ 31.5 – 77.0 days). The activation energy of degradation was in the range of 17 to 28 kJ mol^{-1} and significantly higher for soil with higher pH and lower clay content and iron oxides due to lower catalysis. Soil sterilization caused a 3 to 10–fold decrease in rates compared to non-steriled soils ($t_{½}$ 53.3 – 115.5 days) demonstrating that acephate degradation was mainly governed by microbial processes. At 5–fold increase in application rates (25 μg g^{-1}), the half-life was only increased slightly ($t_{½}$ 13.1 – 19.3 days) for Semongok and Tarat soils but shorter for Balai Ringin soils. Higher methamidophos concentration was detected in non-sterilized soils (< 1.34 mg/kg) as compared to sterilized soils (< 0.02 mg/kg). Half-life from acephate mineralization was similar with those from degradation but longer with increased in application rates ($t_{½}$ 40.8 – 96.3 days). Application of acephate should therefore be restricted and if possible, avoided during wet period with heavy rainfall; especially on flooded soil used for paddy cultivation.